



C₆₀ layer growth on the Co/Si(1 1 1) $\sqrt{7} \times \sqrt{7}$ surface



D.A. Olyanich^{a,b}, T.V. Utas^{a,b}, V.G. Kotlyar^{a,b}, A.V. Zotov^{a,b,c}, A.A. Saranin^{a,b,*},
L.N. Romashev^d, N.I. Solin^d, V.V. Ustinov^d

^a Institute of Automation and Control Processes, 5 Radio Street, 690041 Vladivostok, Russia

^b School of Natural Sciences, Far Eastern Federal University, 690950 Vladivostok, Russia

^c Department of Electronics, Vladivostok State University of Economics and Service, 690600 Vladivostok, Russia

^d Institute of Metal Physics, 620990 Ekaterinburg, Russia

ARTICLE INFO

Article history:

Received 4 August 2013

Received in revised form

11 December 2013

Accepted 13 December 2013

Available online 24 December 2013

PACS:

68.43.Hn

68.37.Ef

68.43.Bc

Keywords:

Atom–solid interactions

Silicon

Fullerene

Self-assembly

Scanning tunneling microscopy

ABSTRACT

The system of C₆₀ layer on Si(1 1 1) $\sqrt{7} \times \sqrt{7}$ -Co surface has a negligible lattice mismatch and with the designed two-step procedure which allows formation of the highly ordered Si(1 1 1) $\sqrt{7} \times \sqrt{7}$ -Co surface with domain size of ~100 nm, one could expect to achieve a perfect epitaxial growth of C₆₀ molecular layer. However, using scanning tunneling microscopy observations we have found that regular C₆₀ arrays grown on such a promising surface typically do not exceed the size of ~10 nm. It has been recognized that the main reason for lacking the long-range ordering in the C₆₀ layer is occurrence of several adsorption sites within the $\sqrt{7} \times \sqrt{7}$ unit cell.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Self-assembly of molecular layers on solid surface has attracted considerable attention motivated by possible applications for molecular-based devices. Among other molecules, the C₆₀ fullerenes are of especial promise due to ability to change their electronic properties depending on the adsorption state. The fullerene-on-silicon system has been found to present a rich set of growth phenomena [1]. Structural properties of the C₆₀ molecular layers are controlled by the interplay between C₆₀-C₆₀ and C₆₀-substrate interactions. On the clean Si(1 1 1) 7×7 , the molecular-substrate interaction prevails, as C₆₀ fullerenes interact with silicon surface via the formation of strong covalent bonds [1]. However, C₆₀ adlayer does not inherit the ordered periodic structure of the Si(1 1 1) 7×7 substrate due to occurrence of various adsorption sites [2–4]. The silicon's surface chemistry can be modified via adsorption of suitable species leading to the

formation of ordered adsorbate-induced Si(1 1 1) reconstructions. For example, the Si(1 1 1) $\sqrt{3} \times \sqrt{3}$ -Ag [5–8], Si(1 1 1) $\sqrt{3} \times \sqrt{3}$ -B [9], and Si(1 1 1) $\sqrt{3} \times \sqrt{3}$ -Au [10] are chemically inert, hence there the C₆₀-C₆₀ van-der-Waals interactions dominate. As a result, fullerenes agglomerate into hexagonal close-packed arrays with a C₆₀ nearest-neighbor distance similar to that in a bulk fullerite, 10.02 Å. Nevertheless, the underlying substrate reconstructions produce certain subtle effects on the structure of molecular layers. For example, the Si(1 1 1) $\sqrt{3} \times \sqrt{3}$ -Au surface induces specific Moiré patterns in the C₆₀ overlayer [10] which cause the size-selection effects in C₆₀ island growth [11], while C₆₀ interactions with Si(1 1 1) $\sqrt{3} \times \sqrt{3}$ -Ag surface lead to occurrence of C₆₀ in different adsorption configurations within the layer [12]. When the surface reconstructions are not stable enough (e.g., In/Si(1 1 1) [13,14] or Pb/Si(1 1 1) [15]), adsorbed C₆₀ molecules perturb their structure by displacing metal atoms and adopting direct strong bonding with Si substrate atoms. In all the known cases with a strong C₆₀ interaction with Si(1 1 1) substrate, C₆₀ molecules are never arranged into an ordered layer dictated by the substrate periodicity. Stable reconstructed Si(1 1 1) surface which periodicity coincides with that of the close-packed C₆₀ layer could be thought to be a promising candidate to reach this goal. The Si(1 1 1) $\sqrt{7} \times$

* Corresponding author at: Institute of Automation and Control Processes, 5 Radio Street, 690041 Vladivostok, Russia. Tel.: +7 4232310426; fax: +7 4232310452.

E-mail address: saranin@iacp.dvo.ru (A.A. Saranin).

$\sqrt{7}$ -R19.1°-Co seems to fit this requirement, since its periodicity of $\sqrt{7}a_0 = 10.16 \text{ \AA}$ (where $a_0 = 3.84 \text{ \AA}$, the lattice constant of the Si(1 1 1) surface) fits within $\sim 1.5\%$ the C_{60} - C_{60} nearest-neighbor distance in a hexagonal close packed C_{60} molecular array (10.02 \AA) and one could expect a perfect epitaxial growth.

It is worth noting that studies of the initial stages of silicide growth in the Co/Si(1 1 1) system have become very extensive in the last years [16–21]. It has been found that structurally very different Co-rich Si(1 1 1) surfaces can be formed depending on the preparation conditions, including so-called “1 × 1”-RC (ring cluster) structure and ordered $\sqrt{7} \times \sqrt{7}$ -R19.1°, $\sqrt{19} \times \sqrt{19}$ -R23.4° and $\sqrt{13} \times \sqrt{13}$ -R13.9° reconstructions. Among them, the $\sqrt{7} \times \sqrt{7}$ -R19.1° is of especially promise, as it can be fabricated all over the sample surface without any other inclusions. Its atomic structure has been established to consist of the ring clusters arranged into the $\sqrt{7} \times \sqrt{7}$ -R19.1° two-dimensional lattice. Each cluster is composed of a single Co atom in a substitutional silicon position under a six Si adatoms ring [22,23]. The $\sqrt{7} \times \sqrt{7}$ -R19.1° surface (hereafter referred to as $\sqrt{7}$ surface) can be considered as a suitable template for subsequent nanostructure growth as demonstrated, for example, for the formation of Au nanocluster arrays with narrow position and size distributions [18].

In this paper, we report a scanning tunneling microscopy (STM) study of C_{60} layer growth on the Co/Si(1 1 1) $\sqrt{7} \times \sqrt{7}$ -R19.1° reconstruction used as a template surface. For improving the epitaxial conditions, we have designed a technique which allows us to fabricate $\sqrt{7}$ surface with extremely large domains (up to $\sim 100 \text{ nm}$ in size), hence to suppress considerably the effect of domain boundaries. Nevertheless, the regular C_{60} arrays grown on such a surface typically do not exceed the size of $\sim 10 \text{ nm}$. It has been elucidated that though C_{60} fullerenes avoid residing atop the ring clusters, there are several possible adsorption sites within the $\sqrt{7} \times \sqrt{7}$ unit cell of which only the so-called “central T_4 ” and “bridge” site ensure formation of regular close-packed C_{60} arrays. Competition between occupation of the various adsorption sites is the main reason for lacking perfect long-range ordering in the C_{60} molecular layer grown on the Co/Si(1 1 1) $\sqrt{7} \times \sqrt{7}$ -R19.1° reconstructed surface.

2. Experimental details

Our experiments were performed with an Omicron STM operating in an ultrahigh vacuum ($\sim 2.5 \times 10^{-8} \text{ Pa}$). Atomically clean Si(1 1 1) 7×7 surfaces were prepared in situ by flashing to 1280 °C after the samples were first outgassed at 650 °C for several hours. Co was deposited from an electron beam evaporator at a rate of 0.07 ML/min. monitored by a quartz microbalance with an estimated error of about 10%. During depositions, vacuum was better than $\sim 6.0 \times 10^{-8} \text{ Pa}$. Temperature was measured using an infrared pyrometer. C_{60} fullerenes (99.92% purity) were sublimated from a resistively heated Mo crucible. For STM observations electrochemically etched tungsten tips cleaned by in situ heating were employed. STM images were acquired at room temperature in the constant-current mode.

3. Results and discussion

Usual procedure to prepare the Co/Si(1 1 1) $\sqrt{7} \times \sqrt{7}$ -R19.1° reconstructed surface included deposition of 0.1–0.2 ML of Co (nominal Co coverage being $1/7 \approx 0.14 \text{ ML}$) onto the atomically clean Si(1 1 1) 7×7 surface held at room temperature (RT) and subsequent annealing at 500–600 °C [18,20,24]. The resultant surface is completely covered by the $\sqrt{7}$ -Co domains having typical sizes of 10–20 nm [18]. Since the domain boundaries break the long-range surface ordering and can serve as traps for deposited atoms or

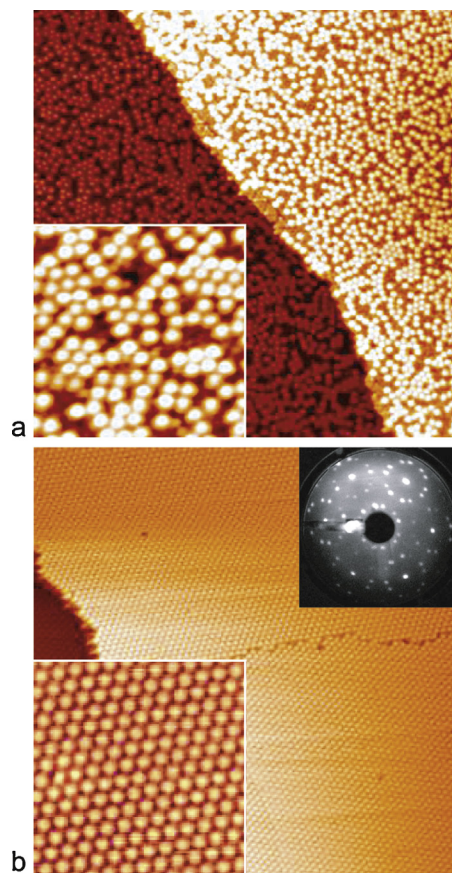


Fig. 1. $800 \times 800 \text{ \AA}^2$ filled-state (-2.0 V) STM images of the (a) intermediate Si(1 1 1)“1 × 1”-RC phase and (b) final Si(1 1 1) $\sqrt{7} \times \sqrt{7}$ -Co surface. Insets show the surface structure at a greater magnification (scale: $120 \times 120 \text{ \AA}^2$). LEED pattern in (b) is taken at 46 eV. Note that Si(1 1 1) $\sqrt{7} \times \sqrt{7}$ reconstruction can occur in two different orientations with rotation angle $R \pm 19.1^\circ$, which eventually generate domain boundaries, as seen in (b).

molecules, it is highly desirable to reduce their density for achieving perfect growth of epitaxial adsorbate layers. We have designed an alternative technique which allows us to prepare the $\sqrt{7}$ -Co surfaces with extremely large domains. This is a two-step procedure when the “1 × 1”-RC phase is formed first by adsorption of ~ 0.05 – 0.10 ML of Co onto Si(1 1 1) 7×7 surface held at about 800 °C, then the temperature is gradually lowered down to 700 °C with continuous Co deposition until the whole surface becomes covered by the $\sqrt{7}$ -Co phase. In the present study, the second stage takes about 3 min, for which time $\sim 0.2 \text{ ML}$ Co was deposited but only required $\sim 0.14 \text{ ML}$ was left at the surface.

As an example, Fig. 1 shows STM images of the intermediate “1 × 1”-RC phase and final $\sqrt{7}$ -reconstructed surface. Both surfaces are composed of RCs with only difference that the “1 × 1”-RC phase appears as a random incomplete RC array containing 0.05–0.1 ML Co, while the $\sqrt{7}$ phase is an ordered close-packed hexagonal array of RCs with $1/7 \text{ ML}$ Co coverage. Being structurally akin to the $\sqrt{7}$ phase, the “1 × 1”-RC surface appears to be a suitable precursor to facilitate formation of the almost perfect $\sqrt{7}$ surface with domain size of up to $\sim 100 \text{ nm}$ (Fig. 1b). Original Si(1 1 1) 7×7 surface does not produce such an effect plausibly because that it is structurally very different from the $\sqrt{7}$ phase and considerable reordering of the top Si substrate layers is required before the $\sqrt{7}$ phase could be built. Thus, using the two-step procedure described above, one obtains highly ordered Si(1 1 1) $\sqrt{7} \times \sqrt{7}$ -Co surfaces like those shown in Figs. 1b and 2a. Besides STM observations, the high structural quality of the surface is proved also by the sharp

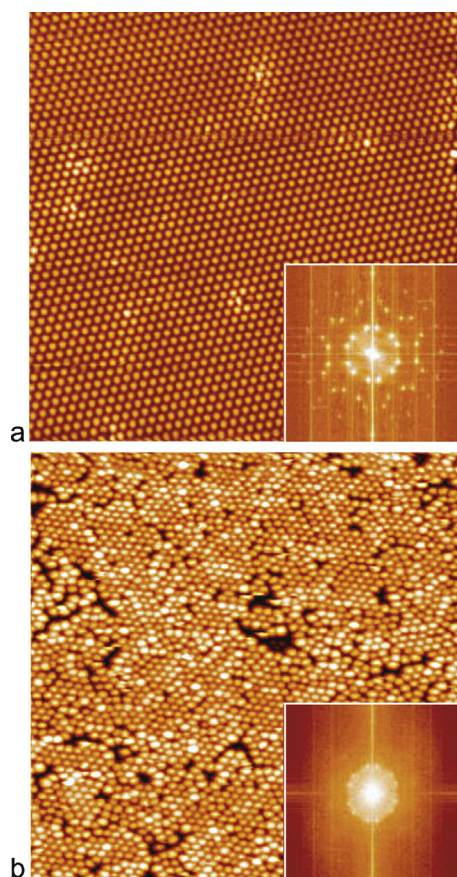


Fig. 2. $500 \times 500 \text{ \AA}^2$ filled-state (-2.0 V) STM images of the $\text{Si}(111)\sqrt{7} \times \sqrt{7}$ surface (a) before and (b) after RT deposition of C_{60} monomolecular layer. Insets show the FFT images taken from the surface areas of greater size ($1000 \times 1000 \text{ \AA}^2$) containing domains of both $R \pm 19.1^\circ$ orientations. The dark regions between fullerenes are spots of bare $\sqrt{7}$ -Co substrate, the difference in STM contrast of C_{60} within the layer is plausibly due to the difference in their adsorption states. Note that almost the whole area of the $\sqrt{7}$ -Co substrate surface shown in (b) corresponds to a single domain.

LEED patterns (inset in Fig. 1b) and FFT images (inset in Fig. 2a). One could expect this surface to be an ideal template for growing C_{60} molecular layers with a long-range ordering.

Fig. 2b illustrates the structure of C_{60} monomolecular layer grown on the well-ordered $\sqrt{7}$ surface held at RT. One can see that the general $\sqrt{7} \times \sqrt{7}$ surface periodicity is preserved (as evidenced, in particular, by the FFT image shown in the inset in Fig. 2b), but actually the long-range ordering is lacking due to the limited size of the regular C_{60} domains. Even within the same $\sqrt{7}$ -Co domain of the substrate surface $\sim 50 \text{ nm}$ in size (as in Fig. 2b), the typical sizes of regular C_{60} domains do not exceed $\sim 10 \text{ nm}$.

To clarify the origin of breaking the long-range ordering in the C_{60} layer, we have considered the earlier stages of C_{60} layer growth. In this case, the C_{60} arrays coexist with the regions of the bare $\sqrt{7}$ -Co substrate surface, that allows us to elucidate the C_{60} adsorption sites on the $\sqrt{7} \times \sqrt{7}$ -Co lattice. Remind that Co-RC consists of six Si adatoms forming ring above a Co atom in substitutional Si position (see Fig. 3d), hence the cluster center corresponds to an on-top (T_1) site [22,23]. As an example, Fig. 3a shows a fragment of such a surface. Fig. 3d shows structural model of the $\sqrt{7} \times \sqrt{7}$ -Co surface with the grid drawn through RCs. Comparison of the experimental images with the model leads to the following conclusions regarding the C_{60} adsorption sites. C_{60} fullerenes definitely avoid residing atop the RCs as their locations never coincide with the grid nodes. When the fullerenes are arranged into the regular close-packed array, they occupy either the “central H_3 ” (Fig. 3c) or

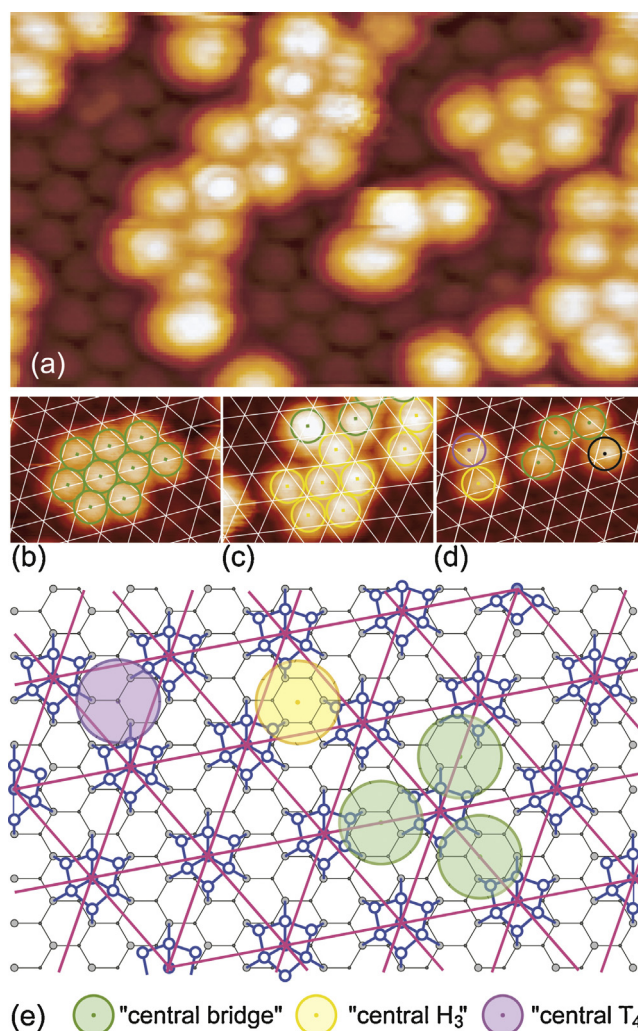


Fig. 3. (a) $115 \times 70 \text{ \AA}^2$ STM image of the $\text{Si}(111)\sqrt{7} \times \sqrt{7}$ -Co surface with uncompleted C_{60} molecular layer. (b) and (c) Regular close-packed C_{60} domains superposed with the grid which nodes coincide with the locations of RCs. The C_{60} fullerenes in (b) and (c) occupy regular “central bridge” and “central H_3 ” sites, respectively. (d) The C_{60} array with fullerenes occupying various adsorption sites, including seldom T_4 and irregular sites (outlined by violet and black circles, respectively). (e) Schematic diagram illustrating regular C_{60} adsorption sites, i.e., “central bridge” (green circles), “central H_3 ” (yellow circle) and “central T_4 ” (violet circle), on the model $\sqrt{7} \times \sqrt{7}$ -Co surface. The RCs are shown in blue, the topmost and second-layer Si atoms of the top Si bilayer are shown by small gray circles and black dots, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

“central bridge” (Fig. 3b) sites. The “central H_3 ” site is located in the center of the one $\sqrt{7}$ half unit cell (triangle pointed up) (Fig. 3e). Fullerene in such a position is shown by yellow circle in the model. The “central bridge” site is that at the center of the diagonal of the $\sqrt{7}$ unit cell in between T_4 and H_3 sites. Fullerenes in the three possible positions of this type are shown by green circles in the model (Fig. 3e). Occurrence probability of regular domains of the both types is almost the same but with a small preference for the domains with C_{60} in the “bridge” sites (occupation ratio being about 4:3). Remarkably, there are no regular domains (and even individual C_{60} are very seldom) with occupation of the “central T_4 ” site. It is located in the center of the $\sqrt{7}$ half unit cell other than that with “central H_3 ” site (triangle pointed down). Fullerene in the “central T_4 ” site is shown in Fig. 3d and e by the violet circles. Besides the C_{60} molecules in one of the above “regular” sites there are also fullerenes in the various non-regular (asymmetric) positions which could hardly be unambiguously identified. As an example, such

a fullerene outlined in black is shown in Fig. 3d. However, these fullerenes together with the seldom ones in the “central T₄” sites constitute in total less than ~10%. As a final remark, we would like to note that adsorption energy in the different sites does not seem to vary much as annealing of the C₆₀ arrays on Si(1 1 1) $\sqrt{7} \times \sqrt{7}$ surface (say, at 150 °C) does not improve noticeably its structural properties.

4. Conclusions

In conclusion, the system of C₆₀ layer on Si(1 1 1) $\sqrt{7} \times \sqrt{7}$ surface looked very promising for achieving a perfect epitaxial growth of molecular layer on metal-induced Si(1 1 1) reconstruction. The lattice mismatch between the C₆₀ layer and Si(1 1 1) $\sqrt{7} \times \sqrt{7}$ substrate is less than 1.5%. Moreover, the designed two-step procedure allows us to fabricate the Si(1 1 1) $\sqrt{7} \times \sqrt{7}$ surface with the domain size of up to ~100 nm, which is thought to be an almost ideal template surface. However, the necessary requirement for the perfect epitaxial growth, i.e. a single preferred adsorption site of C₆₀ within the $\sqrt{7} \times \sqrt{7}$ unit cell, is not fulfilled. It has been found that though C₆₀ fullerenes definitely avoid residing atop the Co-ring clusters constituting the $\sqrt{7} \times \sqrt{7}$ lattice there are still several possible adsorption sites in between the ring clusters. These adsorption sites are plausibly characterized by similar adsorption energies, hence competition between them results in a limited size (~10 nm) of the regular close-packed C₆₀ arrays.

Acknowledgement

Part of this work was supported by the Russian Foundation for Basic Research (Grant nos. 11-02-98515, 11-02-98516, 13-02-00837 and 12-02-00430).

References

- [1] P.J. Moriarty, Surf. Sci. Rep. 65 (2010) 175.
- [2] D. Chen, R.K. Workman, D. Sarid, J. Vac. Sci. Technol. B 14 (1996) 979.
- [3] X. Du, F. Chen, X. Cen, X. Wu, Y. Cai, X. Liu, L. Wang, Appl. Phys. Lett. 97 (2010) 253106.
- [4] R. Ruraili, R. Cuadrado, J.I. Cerdá, Phys. Rev. B 81 (2010) 075419.
- [5] M.D. Upward, P. Moriarty, P.H. Beton, Phys. Rev. B 56 (1997) R1704.
- [6] T. Nakayama, J. Onoe, K. Takeuchi, M. Aono, Phys. Rev. B 59 (1999) 12627.
- [7] K. Tsuchie, T. Nagao, S. Hasegawa, Phys. Rev. B 60 (1999) 11131.
- [8] M. Nakaya, T. Nakayama, Y. Kuwahara, M. Aono, Surf. Sci. 600 (2006) 2810.
- [9] T. Stimpel, M. Schraufstetter, H. Baumgärtner, I. Eisele, Mater. Sci. Eng. B 89 (2002) 394.
- [10] A.V. Matetskiy, D.V. Gruznev, A.V. Zotov, A.A. Saranin, Phys. Rev. B 83 (2011) 195421.
- [11] D.V. Gruznev, A.V. Matetskiy, L.V. Bondarenko, O.A. Utas, A.V. Zotov, A.A. Saranin, J.P. Chou, C.M. Wei, M.Y. Lai, Y.L. Wang, Nat. Commun. 4 (2013) 1679.
- [12] D.V. Gruznev, A.V. Matetskiy, L.V. Bondarenko, A.V. Zotov, A.A. Saranin, J.P. Chou, C.M. Wei, Y.L. Wang, Surf. Sci. 612 (2013) 31.
- [13] D.V. Gruznev, A.V. Matetskiy, I.V. Gvozdz, A.V. Zotov, A.A. Saranin, Surf. Sci. 605 (2011) 1951.
- [14] V.G. Kotlyar, D.A. Olyanich, T.V. Utas, A.V. Zotov, A.A. Saranin, Surf. Sci. 606 (2012) 1821.
- [15] A.V. Matetskiy, L.V. Bondarenko, D.V. Gruznev, A.V. Zotov, A.A. Saranin, M.C. Tringides, J. Phys.: Condens. Matter 25 (2013) 395006.
- [16] M. Löffler, J. Cordón, M. Weinelt, J.E. Ortega, T. Fauster, Appl. Phys. A 81 (2005) 1651.
- [17] Y.T. Cui, T. Xie, M. Ye, A. Kimura, S. Qiao, H. Namatame, M. Taniguchi, Appl. Surf. Sci. 254 (2008) 7684.
- [18] F. Dulot, M.C. Hanf, P. Wetzel, Surf. Sci. 602 (2008) 1447.
- [19] L. Chaput, F. Dulot, M.C. Hanf, P. Wetzel, Surf. Sci. 604 (2010) 513.
- [20] M. Odagiri, I. Mochizuki, Y. Shigeta, A. Tosaka, Appl. Phys. Lett. 97 (2010) 151911.
- [21] Z. Yuan, P. Sonnet, M.C. Hanf, R. Stephan, F. Dulot, P. Wetzel, Surf. Sci. 607 (2013) 111.
- [22] P.A. Bennett, M. Copel, D. Cahill, J. Falta, R.M. Tromp, Phys. Rev. Lett. 69 (1992) 1224.
- [23] M.H. Tsai, J.D. Dow, P.A. Bennett, D.G. Cahill, Phys. Rev. B 48 (1993) 2486.
- [24] A.E. Dolbak, B.Z. Olshanetsky, S.A. Teys, Surf. Sci. 373 (1997) 43.